Detailed Phonon Dynamics Approach Reveals Origins of the Hot Carrier Effect in Perovskites

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Semiconductor materials relying on the hybrid organic-inorganic perovskites have been exhibiting impressive photovoltaic device performances, due to long electronics carrier diffusion lengths, low exciton binding energy, high absorption coefficient and low thermal conductance [1]. Extensive work has been done in exploring additional promising features of these materials, namely, the hot carrier effect [2,3]. Several mechanisms for the explanation of the effect have been proposed, most of which outline the importance of the electron-phonon and phonon-phonon interactions that induce the non-equilibrium phonon population to act as a thermal reservoir to reheat the electrons thus extending their lifetime.

Our recent results also indicate long carrier lifetimes and hence propose a model that suggests a complex interplay between organic/inorganic optical and acoustic phonon modes that result in the confinement of the lowest energy acoustic modes and their subsequent up-conversion and reabsorption by higher energy modes and eventually by hot carriers, significantly extending the lifetime of the latter [4]. However, in order to assess that hypothesis, an adequate understanding of phonon dynamics in addition to currently, well-understood electron dynamic is necessary. Thus, we choose neutron scattering over the other inelastic scattering techniques (due to much higher energy resolution achievable) to investigate the phonon contribution to the hot carrier effect.

We perform measurements on deuterated methylammonium lead iodide (D-MAPI) single crystal perovskite at ANSTO, using both cold and thermal triple axis spectrometer (SIKA and TAIPAN, respectively). We map the phonon dispersion (Figure 1) and for the first time observe well resolved optical modes at lower temperatures. We determine momentum resolved lifetimes of both acoustic and optical phonons at three different crystal phases.

Preliminary results also indicate the presence of non-equilibrium transverse acoustic phonons by measuring their occupancy number and creation and annihilation lifetimes in various directions in the Brillouin zone (Figure 2). This may be the clear experimental evidence for the previously proposed hypothesis of acoustic up conversion. Namely, it is evident that the population of TA modes is less than in equilibrium which indicates that those phonons must be scattering elsewhere. As TA modes occupy the lowest energy phonon band the only scattering path is towards higher energies.

Furthermore we observe strong phonon dumping when the system undergoes order to disorder transition (orthorhombic to tetragonal phase) which is an indication of a coupling of the organic cation with other phonon modes (Figure 3). Moreover, acoustic phonon lifetimes at room temperature are an order of magnitude lower than expected, leading to the conclusion that their inability to dissipate heat from the system leads to their up-conversion which we eventually observe through long-lived hot carrier population.
Figure 1. Measured phonon dispersion (dots) and DFT predicted dispersion (lines)

\[ q=\begin{pmatrix} 0 & 0 & 2.05 \end{pmatrix} \]

Figure 2. Fitted INS data indicating the evidence of phonon up-conversion

Figure 3. Temperature dependent acoustic and optical phonon lifetimes

